

1

Introduction

Surface active agents (usually referred to as surfactants) are amphipathic molecules that consist of a non-polar hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8–18 carbon atoms, which is attached to a polar or ionic portion (hydrophilic). The hydrophilic portion can, therefore, be nonionic, ionic or zwitterionic, and accompanied by counter ions in the last two cases. The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion–dipole interactions. It is this strong interaction with the water molecules that renders the surfactant soluble in water. However, the cooperative action of dispersion and hydrogen bonding between the water molecules tends to squeeze the hydrocarbon chain out of the water and hence these chains are referred to as hydrophobic. As we will see later, the balance between hydrophobic and hydrophilic parts of the molecule gives these systems their special properties, e.g. accumulation at various interfaces and association in solution (to form micelles).

The driving force for surfactant adsorption is the lowering of the free energy of the phase boundary. As we will see in later chapters, the interfacial free energy per unit area is the amount of work required to expand the interface. This interfacial free energy, referred to as surface or interfacial tension, γ , is given in mJ m^{-2} or mN m^{-1} . Adsorption of surfactant molecules at the interface lowers γ , and the higher the surfactant adsorption (i.e. the denser the layer) the larger the reduction in γ . The degree of surfactant adsorption at the interface depends on surfactant structure and the nature of the two phases that meet the interface [1, 2].

As noted, surface active agents also aggregate in solution forming micelles. The driving force for micelle formation (or micellization) is the reduction of contact between the hydrocarbon chain and water, thereby reducing the free energy of the system (see Chapter 2). In the micelle, the surfactant hydrophobic groups are directed towards the interior of the aggregate and the polar head groups are directed towards the solvent. These micelles are in dynamic equilibrium and the rate of exchange between a surfactant molecule and the micelle may vary by orders of magnitude, depending on the structure of the surfactant molecule.

Surfactants find application in almost every chemical industry, including detergents, paints, dyestuffs, cosmetics, pharmaceuticals, agrochemicals, fibres, plastics.

Moreover, surfactants play a major role in the oil industry, for example in enhanced and tertiary oil recovery. They are also occasionally used for environmental protection, e.g. in oil slick dispersants. Therefore, a fundamental understanding of the physical chemistry of surface active agents, their unusual properties and their phase behaviour is essential for most industrial chemists. In addition, an understanding of the basic phenomena involved in the application of surfactants, such as in the preparation of emulsions and suspensions and their subsequent stabilization, in microemulsions, in wetting spreading and adhesion, etc., is of vital importance in arriving at the right composition and control of the system involved [1, 2]. This is particularly the case with many formulations in the chemical industry.

Commercially produced surfactants are not pure chemicals, and within each chemical type there can be tremendous variation. This is understandable since surfactants are prepared from various feedstocks, namely petrochemicals, natural vegetable oils and natural animal fats. Notably, in every case the hydrophobic group exists as a mixture of chains of different lengths. The same applies to the polar head group, for example with poly(ethylene oxide) (the major component of non-ionic surfactants), which consists of a distribution of ethylene oxide units. Hence, products that may be given the same generic name could vary a great deal in their properties, and the formulation chemist should bear this in mind when choosing a surfactant from a particular manufacturer. It is advisable to obtain as much information as possible from the manufacturer about the properties of the surfactant chosen, such as its suitability for the job, its batch to batch variation, toxicity, etc. The manufacturer usually has more information on the surfactant than that printed in the data sheet, and in most cases such information is given on request.

1.1

General Classification of Surface Active Agents

A simple classification of surfactants based on the nature of the hydrophilic group is commonly used. Three main classes may be distinguished, namely anionic, cationic and amphoteric. A useful technical reference is McCutcheon [3], which is produced annually to update the list of available surfactants. van Os et al. have listed the physicochemical properties of selected anionic, cationic and nonionic surfactants [4]. Another useful text is the *Handbook of Surfactants* by Porter [5]. In addition, a fourth class of surfactants, usually referred to as polymeric surfactants, has long been used for the preparation of emulsions and suspensions and their stabilization.

1.2

Anionic Surfactants

These are the most widely used class of surfactants in industrial applications [6, 7] due to their relatively low cost of manufacture and they are used in practically every

type of detergent. For optimum detergency the hydrophobic chain is a linear alkyl group with a chain length in the region of 12–16 carbon atoms. Linear chains are preferred since they are more effective and more degradable than branched ones. The most commonly used hydrophilic groups are carboxylates, sulphates, sulphonates and phosphates. A general formula may be ascribed to anionic surfactants as follows:

- Carboxylates: $C_nH_{2n+1}COO^-X$
- Sulphates: $C_nH_{2n+1}OSO_3^-X$
- Sulphonates: $C_nH_{2n+1}SO_3^-X$
- Phosphates: $C_nH_{2n+1}OPO(OH)O^-X$

with $n = 8$ –16 atoms and the counter ion X is usually Na^+ .

Several other anionic surfactants are commercially available such as sulphosuccinates, isethionates and taurates and these are sometimes used for special applications. These anionic classes and some of their applications are briefly described below.

1.2.1

Carboxylates

These are perhaps the earliest known surfactants since they constitute the earliest soaps, e.g. sodium or potassium stearate, $C_{17}H_{35}COONa$, sodium myristate, $C_{14}H_{29}COONa$. The alkyl group may contain unsaturated portions, e.g. sodium oleate, which contains one double bond in the C_{17} alkyl chain. Most commercial soaps are a mixture of fatty acids obtained from tallow, coconut oil, palm oil, etc. The main attraction of these simple soaps is their low cost, their ready biodegradability and low toxicity. Their main disadvantages are their ready precipitation in water containing bivalent ions such as Ca^{2+} and Mg^{2+} . To avoid such precipitation in hard water, the carboxylates are modified by introducing some hydrophilic chains, e.g. ethoxy carboxylates with the general structure $RO(CH_2CH_2O)_nCH_2COO^-$, ester carboxylates containing hydroxyl or multi $COOH$ groups, sarcosinates which contain an amide group with the general structure $RCON(R')COO^-$.

The addition of the ethoxylated groups increases water solubility and enhances chemical stability (no hydrolysis). The modified ether carboxylates are also more compatible both with electrolytes and with other nonionic, amphoteric and sometimes even cationic surfactants. The ester carboxylates are very soluble in water, but undergo hydrolysis. Sarcosinates are not very soluble in acid or neutral solutions but are quite soluble in alkaline media. They are compatible with other anionics, nonionics and cationics. Phosphate esters have very interesting properties being intermediate between ethoxylated nonionics and sulphated derivatives. They have good compatibility with inorganic builders and they can be good emulsifiers. A specific salt of a fatty acid is lithium 12-hydroxystearic acid, which forms the major constituent of greases.

1.2.2

Sulphates

These are the largest and most important class of synthetic surfactants, which were produced by reaction of an alcohol with sulphuric acid, i.e. they are esters of sulphuric acid. In practice, sulphuric acid is seldom used and chlorosulphonic or sulphur dioxide/air mixtures are the most common methods of sulphating the alcohol. However, due to their chemical instability (hydrolysing to the alcohol, particularly in acid solutions), they are now overtaken by the chemically stable sulphonates.

The properties of sulphate surfactants depend on the nature of the alkyl chain and the sulphate group. The alkali metal salts show good solubility in water, but tend to be affected by the presence of electrolytes. The most common sulphate surfactant is sodium dodecyl sulphate (abbreviated as SDS and sometimes referred to as sodium lauryl sulphate), which is extensively used both for fundamental studies as well as in many industrial applications. At room temperature ($\sim 25^\circ\text{C}$) this surfactant is quite soluble and 30% aqueous solutions are fairly fluid (low viscosity). However, below 25°C , the surfactant may separate out as a soft paste as the temperature falls below its Krafft point (the temperature above which the surfactant shows a rapid increase in solubility with further increase of temperature). The latter depends on the distribution of chain lengths in the alkyl chain – the wider the distribution the lower the Krafft temperature. Thus, by controlling this distribution one may achieve a Krafft temperature of $\sim 10^\circ\text{C}$. As the surfactant concentration is increased to 30–40% (depending on the distribution of chain length in the alkyl group), the viscosity of the solution increases very rapidly and may produce a gel. The critical micelle concentration (c.m.c.) of SDS (the concentration above which the properties of the solution show abrupt changes) is $8 \times 10^{-3} \text{ mol dm}^{-3}$ (0.24%).

As with the carboxylates, the sulphate surfactants are also chemically modified to change their properties. The most common modification is to introduce some ethylene oxide units in the chain, usually referred to as alcohol ether sulphates, e.g. sodium dodecyl 3-mole ether sulphate, which is essentially dodecyl alcohol reacted with 3 moles EO then sulphated and neutralised by NaOH. The presence of PEO confers improved solubility than for straight alcohol sulphates. In addition, the surfactant becomes more compatible with electrolytes in aqueous solution. Ether sulphates are also more chemically stable than the alcohol sulphates. The c.m.c. of the ether sulphates is also lower than the corresponding surfactant without EO units.

1.2.3

Sulphonates

With sulphonates, the sulphur atom is directly attached to the carbon atom of the alkyl group, giving the molecule stability against hydrolysis, when compared with the sulphates (whereby the sulphur atom is indirectly linked to the carbon of the hydrophobe via an oxygen atom). Alkyl aryl sulphonates are the most common

type of these surfactants (e.g. sodium alkyl benzene sulphonate) and these are usually prepared by reaction of sulphuric acid with alkyl aryl hydrocarbons, e.g. dodecyl benzene. A special class of sulphonate surfactants is the naphthalene and alkyl naphthalene sulphonates, which are commonly used as dispersants.

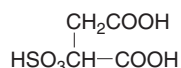
As with the sulphates, some chemical modification is used by introducing ethylene oxide units, e.g. sodium nonyl phenol 2-mole ethoxylate ethane sulphonate, $\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_2\text{SO}_3^- \text{Na}^+$.

Paraffin sulphonates are produced by sulpho-oxidation of normal linear paraffins with sulphur dioxide and oxygen and catalyzed with ultraviolet or gamma radiation. The resulting alkane sulphononic acid is neutralized with NaOH. These surfactants have excellent water solubility and biodegradability. They are also compatible with many aqueous ions.

Linear alkyl benzene sulphonates (LABS) are manufactured from alkyl benzene, and the alkyl chain length can vary from C_8 to C_{15} ; their properties are mainly influenced by the average molecular weight and the spread of carbon number of the alkyl side chain. The c.m.c. of sodium dodecyl benzene sulphonate is $5 \times 10^{-3} \text{ mol dm}^{-3}$ (0.18%). The main disadvantages of LABS are their effect on the skin and hence they cannot be used in personal care formulations.

Another class of sulphonates is the α -olefin sulphonates, which are prepared by reacting linear α -olefin with sulphur trioxide, typically yielding a mixture of alkene sulphonates (60–70%), 3- and 4-hydroxyalkane sulphonates (~30%) and some disulphonates and other species. The two main α -olefin fractions used as starting material are C_{12} – C_{16} and C_{16} – C_{18} .

A special class of sulphonates is the sulphosuccinates, which are esters of sulphosuccinic acid (1.1).



1.1

Both mono and diesters are produced. A widely used diester in many formulations is sodium di(2-ethylhexyl)sulphosuccinate (sold commercially under the trade name Aerosol OT). The diesters are soluble both in water and in many organic solvents. They are particularly useful for preparation of water-in-oil (W/O) micro-emulsions (Chapter 10).

1.2.4

Phosphate-containing Anionic Surfactants

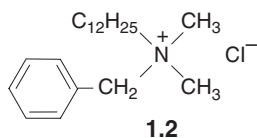
Both alkyl phosphates and alkyl ether phosphates are made by treating the fatty alcohol or alcohol ethoxylates with a phosphorylating agent, usually phosphorous pentoxide, P_4O_{10} . The reaction yields a mixture of mono- and di-esters of phosphoric acid. The ratio of the two esters is determined by the ratio of the reactants and the amount of water present in the reaction mixture. The physicochemical

properties of the alkyl phosphate surfactants depend on the ratio of the esters. Phosphate surfactants are used in the metal working industry due to their anti-corrosive properties.

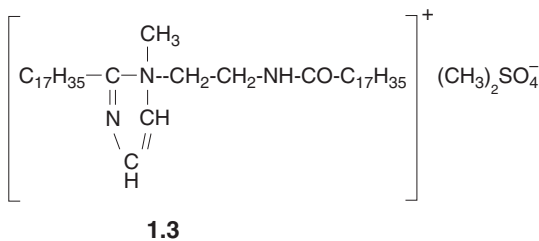
1.3

Cationic Surfactants

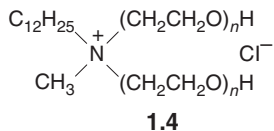
The most common cationic surfactants are the quaternary ammonium compounds [8, 9] with the general formula $R'R''R'''R''''N^+X^-$, where X^- is usually chloride ion and R represents alkyl groups. A common class of cationics is the alkyl trimethyl ammonium chloride, where R contains 8–18 C atoms, e.g. dodecyl trimethyl ammonium chloride, $C_{12}H_{25}(CH_3)_3NCl$. Another widely used cationic surfactant class is that containing two long-chain alkyl groups, i.e. dialkyl dimethyl ammonium chloride, with the alkyl groups having a chain length of 8–18 C atoms. These dialkyl surfactants are less soluble in water than the monoalkyl quaternary compounds, but they are commonly used in detergents as fabric softeners. A widely used cationic surfactant is alkyl dimethyl benzyl ammonium chloride (sometimes referred to as benzalkonium chloride and widely used as bactericide) (1.2).



Imidazolines can also form quaternaries, the most common product being the ditalow derivative quaternized with dimethyl sulphate (1.3).



Cationic surfactants can also be modified by incorporating poly(ethylene oxide) chains, e.g. dodecyl methyl poly(ethylene oxide) ammonium chloride (1.4).



Cationic surfactants are generally water soluble when there is only one long alkyl group. They are generally compatible with most inorganic ions and hard water, but they are incompatible with metasilicates and highly condensed phosphates. They are also incompatible with protein-like materials. Cationics are generally stable to pH changes, both acid and alkaline. They are incompatible with most anionic surfactants, but they are compatible with nonionics. These cationic surfactants are insoluble in hydrocarbon oils. In contrast, cationics with two or more long alkyl chains are soluble in hydrocarbon solvents, but they become only dispersible in water (sometimes forming bilayer vesicle type structures). They are generally chemically stable and can tolerate electrolytes. The c.m.c. of cationic surfactants is close to that of anionics with the same alkyl chain length.

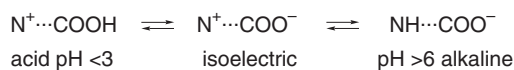
The prime use of cationic surfactants is their tendency to adsorb at negatively charged surfaces, e.g. anticorrosive agents for steel, flotation collectors for mineral ores, dispersants for inorganic pigments, antistatic agents for plastics, other antistatic agents and fabric softeners, hair conditioners, anticaking agent for fertilizers and as bactericides.

1.4

Amphoteric (Zwitterionic) Surfactants

These are surfactants containing both cationic and anionic groups [10]. The most common amphoterics are the N-alkyl betaines, which are derivatives of trimethyl glycine $(\text{CH}_3)_3\text{NCH}_2\text{COOH}$ (described as betaine). An example of betaine surfactant is lauryl amido propyl dimethyl betaine $\text{C}_{12}\text{H}_{25}\text{CON}(\text{CH}_3)_2\text{CH}_2\text{COOH}$. These alkyl betaines are sometimes described as alkyl dimethyl glycinate.

The main characteristic of amphoteric surfactants is their dependence on the pH of the solution in which they are dissolved. In acid pH solutions, the molecule acquires a positive charge and behaves like a cationic surfactant, whereas in alkaline pH solutions they become negatively charged and behave like an anionic one. A specific pH can be defined at which both ionic groups show equal ionization (the isoelectric point of the molecule) (described by Scheme 1.1).



Scheme 1.1

Amphoteric surfactants are sometimes referred to as zwitterionic molecules. They are soluble in water, but the solubility shows a minimum at the isoelectric point. Amphoterics show excellent compatibility with other surfactants, forming mixed micelles. They are chemically stable both in acids and alkalis. The surface activity of amphoterics varies widely and depends on the distance between the charged groups, showing maximum activity at the isoelectric point.

Another class of amphoteric surfactants is the N-alkyl amino propionates having the structure $R-NHCH_2CH_2COOH$. The NH group can react with another acid molecule (e.g. acrylic) to form an amino dipropionate $R-N(CH_2CH_2COOH)_2$. Alkyl imidazoline-based products can also be produced by reacting alkyl imidazoline with a chloro acid. However, the imidazoline ring breaks down during the formation of the amphoteric.

The change in charge with pH of amphoteric surfactants affects their properties, such as wetting, detergency, foaming, etc. At the isoelectric point (i.e.p.), the properties of amphoteric surfactants resemble those of non-ionics very closely. Below and above the i.e.p. the properties shift towards those of cationic and anionic surfactants, respectively. Zwitterionic surfactants have excellent dermatological properties. They also exhibit low eye irritation and are frequently used in shampoos and other personal care products (cosmetics).

1.5

Nonionic Surfactants

The most common nonionic surfactants are those based on ethylene oxide, referred to as ethoxylated surfactants [11–13]. Several classes can be distinguished: alcohol ethoxylates, alkyl phenol ethoxylates, fatty acid ethoxylates, monoalkanolamide ethoxylates, sorbitan ester ethoxylates, fatty amine ethoxylates and ethylene oxide–propylene oxide copolymers (sometimes referred to as polymeric surfactants).

Another important class of nonionics is the multihydroxy products such as glycol esters, glycerol (and polyglycerol) esters, glucosides (and polyglucosides) and sucrose esters. Amine oxides and sulphinyl surfactants represent nonionics with a small head group.

1.5.1

Alcohol Ethoxylates

These are generally produced by ethoxylation of a fatty chain alcohol such as dodecanol. Several generic names are given to this class of surfactants, such as ethoxylated fatty alcohols, alkyl polyoxyethylene glycol, monoalkyl poly(ethylene oxide) glycol ethers, etc. A typical example is dodecyl hexaoxyethylene glycol monoether with the chemical formula $C_{12}H_{25}(OCH_2CH_2O)_6OH$ (sometimes abbreviated as $C_{12}E_6$). In practice, the starting alcohol will have a distribution of alkyl chain lengths and the resulting ethoxylate will have a distribution of ethylene oxide chain lengths. Thus the numbers listed in the literature refer to average numbers.

The c.m.c. of nonionic surfactants is about two orders of magnitude lower than the corresponding anionics with the same alkyl chain length. The solubility of the alcohol ethoxylates depends both on the alkyl chain length and the number of ethylene oxide units in the molecule. Molecules with an average alkyl chain length

of 12 C atoms and containing more than 5 EO units are usually soluble in water at room temperature. However, as the temperature of the solution is gradually raised the solution becomes cloudy (due to dehydration of the PEO chain) and the temperature at which this occurs is referred to as the cloud point (C.P.) of the surfactant. At a given alkyl chain length, C.P. increases with increasing EO chain of the molecule. C.P. changes with changing concentration of the surfactant solution and the trade literature usually quotes the C.P. of a 1% solution. The C.P. is also affected by the presence of electrolyte in the aqueous solution. Most electrolytes lower the C.P. of a nonionic surfactant solution. Nonionics tend to have maximum surface activity near to the cloud point. The C.P. of most nonionics increases markedly on the addition of small quantities of anionic surfactants. The surface tension of alcohol ethoxylate solutions decreases with a decrease in the EO units of the chain. The viscosity of a nonionic surfactant solution increases gradually with an increase in its concentration, but at a critical concentration (which depends on the alkyl and EO chain length) the viscosity increases rapidly and, ultimately, a gel-like structure appears owing to the formation of a hexagonal type liquid crystalline structure. In many cases, the viscosity reaches a maximum, after which it decreases due to the formation of other structures (e.g. lamellar phases) (see Chapter 3).

1.5.2

Alkyl Phenol Ethoxylates

These are prepared by reaction of ethylene oxide with the appropriate alkyl phenol. The most common such surfactants are those based on nonyl phenol. These surfactants are cheap to produce, but suffer from biodegradability and potential toxicity (the by-product of degradation is nonyl phenol, which has considerable toxicity). Despite these problems, nonyl phenol ethoxylates are still used in many industrial properties, owing to their advantageous properties, such as their solubility both in aqueous and non-aqueous media, good emulsification and dispersion properties, etc.

1.5.3

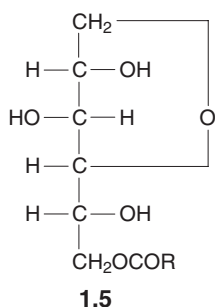
Fatty Acid Ethoxylates

These are produced by reaction of ethylene oxide with a fatty acid or a polyglycol and have the general formula $\text{RCOO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$. When a polyglycol is used, a mixture of mono- and di-esters ($\text{RCOO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{-OCOR}$) is produced. These surfactants are generally soluble in water provided there are enough EO units and the alkyl chain length of the acid is not too long. The mono-esters are much more soluble in water than the di-esters. In the latter case, a longer EO chain is required to render the molecule soluble. The surfactants are compatible with aqueous ions, provided there is not much unreacted acid. However, these surfactants undergo hydrolysis in highly alkaline solutions.

1.5.4

Sorbitan Esters and Their Ethoxylated Derivatives (Spans and Tweens)

Fatty acid esters of sorbitan (generally referred to as Spans, an Atlas commercial trade name) and their ethoxylated derivatives (generally referred to as Tweens) are perhaps one of the most commonly used nonionics. They were first commercialised by Atlas in the USA, which has since been purchased by ICI. The sorbitan esters are produced by reacting sorbitol with a fatty acid at a high temperature ($> 200\text{ }^{\circ}\text{C}$). The sorbitol dehydrates to 1,4-sorbitan and then esterification takes place. If one mole of fatty acid is reacted with one mole of sorbitol, one obtains a mono-ester (some di-ester is also produced as a by-product). Thus, sorbitan mono-ester has the general formula shown in structure 1.5.



The free OH groups in the molecule can be esterified, producing di- and tri-esters. Several products are available depending on the nature of the alkyl group of the acid and whether the product is a mono-, di- or tri-ester. Some examples are given below:

- Sorbitan monolaurate – Span 20
- Sorbitan monopalmitate – Span 40
- Sorbitan monostearate – Span 60
- Sorbitan mono-oleate – Span 80
- Sorbitan tristearate – Span 65
- Sorbitan trioleate – Span 85

Ethoxylated derivatives of Spans (Tweens) are produced by the reaction of ethylene oxide on any hydroxyl group remaining on the sorbitan ester group. Alternatively, the sorbitol is first ethoxylated and then esterified. However, the final product has different surfactant properties to the Tweens. Some examples of Tween surfactants are given below.

- Polyoxyethylene (20) sorbitan monolaurate – Tween 20
- Polyoxyethylene (20) sorbitan monopalmitate – Tween 40

- Polyoxyethylene (20) sorbitan monostearate – Tween 60
- Polyoxyethylene (20) sorbitan mono-oleate – Tween 80
- Polyoxyethylene (20) sorbitan tristearate – Tween 65
- Polyoxyethylene (20) sorbitan tri-oleate – Tween 85

The sorbitan esters are insoluble in water, but soluble in most organic solvents (low HLB number surfactants). The ethoxylated products are generally soluble in water and have relatively high HLB numbers. One of the main advantages of the sorbitan esters and their ethoxylated derivatives is their approval as food additives. They are also widely used in cosmetics and some pharmaceutical preparations.

1.5.5

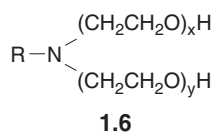
Ethoxylated Fats and Oils

Several natural fats and oils have been ethoxylated, e.g. linolin (wool fat) and caster oil ethoxylates. These products are useful for pharmaceutical products, e.g. as solubilizers.

1.5.6

Amine Ethoxylates

These are prepared by addition of ethylene oxide to primary or secondary fatty amines. With primary amines both hydrogen atoms on the amine group react with ethylene oxide and, therefore, the resulting surfactant has the structure **1.6**.



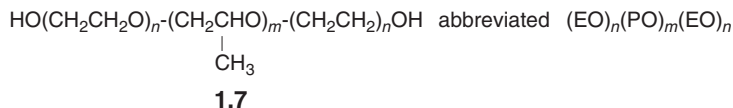
The above surfactants acquire a cationic character if there are few EO units and if the pH is low. However, at high EO levels and neutral pH they behave very similarly to nonionics. At low EO content, the surfactants are not soluble in water, but become soluble in an acid solution. At high pH, the amine ethoxylates are water soluble provided the alkyl chain length of the compound is not long (usually a C₁₂ chain is adequate for reasonable solubility at sufficient EO content).

1.5.7

Ethylene Oxide–Propylene Oxide Co-polymers (EO/PO)

As mentioned above, these may be regarded as polymeric surfactants. These surfactants are sold under various trade names, namely Pluronics (Wyandotte), Synperonic PE (ICI), Poloxamers, etc. Two types may be distinguished: those prepared

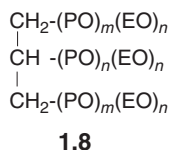
by reaction of poly(oxypropylene glycol) (difunctional) with EO or mixed EO/PO, giving block copolymers (1.7).



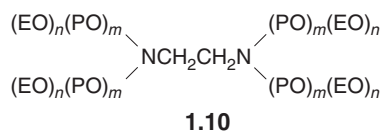
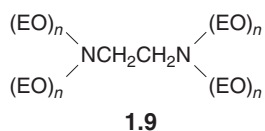
Various molecules are available, where n and m are varied systematically.

The second type of EO/PO copolymers are prepared by reaction of poly(ethylene glycol) (difunctional) with PO or mixed EO/PO. These will have the structure $(\text{PO})_n(\text{EO})_m(\text{PO})_n$ and are referred to as reverse Pluronics.

Trifunctional products (1.8) are also available where the starting material is glycerol.



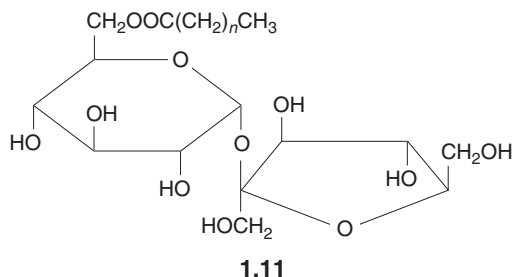
Tetrafunctional products (1.9 and 1.10) are available where the starting material is ethylene diamine.



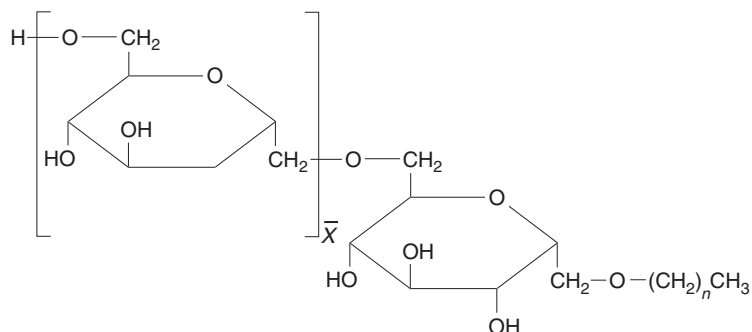
1.5.8

Surfactants Derived from Mono- and Polysaccharides

Several surfactants have been synthesized starting from mono- or oligosaccharides by reaction with the multifunctional hydroxyl groups. The technical problem is one of joining a hydrophobic group to the multihydroxyl structure. Several surfactants have been made, e.g. esterification of sucrose with fatty acids or fatty glycerides to produce sucrose esters (1.11).



The most interesting sugar surfactants are the alkyl polyglucosides (APG) (1.12).



1.12

These are produced by reaction of a fatty alcohol directly with glucose. The basic raw materials are glucose and fatty alcohols (which may be derived from vegetable oils) and hence these surfactants are sometimes referred to as “environmentally friendly”. A product with $n = 2$ has two glucose residues with four OH groups on each molecule (i.e. a total of 8 OH groups). The chemistry is more complex and commercial products are mixtures with $n = 1.1\text{--}3$. The properties of APG surfactants depend upon the alkyl chain length and the average degree of polymerisation. APG surfactants have good solubility in water and high cloud points ($> 100\text{ }^{\circ}\text{C}$). They are stable in neutral and alkaline solutions but are unstable in strong acid solutions. APG surfactants can tolerate high electrolyte concentrations and are compatible with most types of surfactants.

1.6

Speciality Surfactants – Fluorocarbon and Silicone Surfactants

These surfactants can lower the surface tension of water to below 20 mN m^{-1} (most surfactants described above lower the surface tension of water to values above 20 mN m^{-1} , typically in the region of $25\text{--}27\text{ mN m}^{-1}$). Fluorocarbon and silicone surfactants are sometimes referred to as superwetters as they cause enhanced wetting and spreading of their aqueous solution. However, they are much more expensive than conventional surfactants and are only applied for specific applications whereby the low surface tension is a desirable property.

Fluorocarbon surfactants have been prepared with various structures, consisting of perfluoroalkyl chains and anionic, cationic, amphoteric and poly(ethylene oxide) polar groups. These surfactants have good thermal and chemical stability and they are excellent wetting agents for low energy surfaces.

Silicone surfactants, sometimes referred to as organosilicones, are those with a poly(dimethyl siloxane) backbone. They are prepared by incorporation of a water-soluble or hydrophilic group into a siloxane backbone. The latter can also be

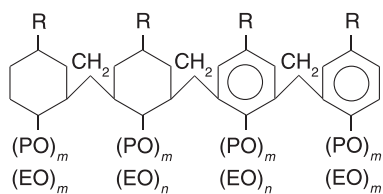
modified by incorporation of a paraffinic hydrophobic chain at the end or along the polysiloxane back bone. The most common hydrophilic groups are EO/PO and the structures produced are rather complex and most manufacturers of silicone surfactants do not reveal the exact structure. The mechanism by which these molecules lower the surface tension of water to low values is far from well understood. The surfactants are widely applied as spreading agents on many hydrophobic surfaces.

Incorporating organophilic groups into the backbone of the poly(dimethyl siloxane) backbone can give products that exhibit surface active properties in organic solvents.

1.7 Polymeric Surfactants

There has been considerable recent interest in polymeric surfactants due to their wide application as stabilizers for suspensions and emulsions. Various polymeric surfactants have been introduced and they are marketed under special trade names (such as Hypermers of ICI). One may consider the block EO/PO molecules (Pluronic) as polymeric surfactants, but these generally do not have high molecular weights and they seldom produce speciality properties. Silicone surfactants may also be considered as polymeric. However, the recent development of speciality polymeric surfactants of the graft type (“comb” structures) have enabled one to obtain specific applications in dispersions. An example is the graft copolymer of a poly(methyl methacrylate) backbone with several PEO side chains (sold under the trade name Hypermer CG6 by ICI), which has excellent dispersing and stabilizing properties for concentrated dispersions of hydrophobic particles in water. Using such a dispersant, one can obtain highly stable concentrated suspensions. These surfactants have been modified in several ways to produce molecules that are suitable as emulsifiers, dispersants in extreme conditions such as high or low pH, high electrolyte concentrations, temperatures etc. Other polymeric surfactants that are suitable for dispersing dyes and pigments in non-aqueous media have also been prepared, whereby the side chains were made oil soluble, such as polyhydroxystearic acid.

Another important class of polymeric surfactants that are used for demulsification is those based on alkoxyated alkyl phenol formaldehyde condensates, with the general structure 1.13.



1.13

Several other complex polymerics are manufactured for application in the oil industry, e.g. polyalkylene glycol modified polyester with fatty acid hydrophobes, polyesters, made by polymerization of polyhydroxy stearic acid, etc.

1.8

Toxicological and Environmental Aspects of Surfactants

1.8.1

Dermatological Aspects

A large fraction of dermatological problems in normal working life can be related to exposure of unprotected skin to surfactant solutions [2]. Several formulations contain significant amount of surfactants, e.g. cutting fluids, rolling oil emulsions, some household cleaning formulations and some personal care products. Skin irritation of various degrees of seriousness is common, and in some cases allergic reactions may also appear. The physiological aspects of surfactants on the skin have been investigated by various dermatological laboratories, starting with the surface of the skin and progressing via the horny layer and its barrier function to the deeper layer of the basal cells. Surfactant classes that are generally known to be mild to the skin include polyol surfactants (alkyl polyglucosides), zwitterionic surfactants (betaines, amidobetaines and isethionates) and many polymeric surfactants. Alcohol ethoxylates are relatively mild, but not as mild as the polyol based non-ionics (the alkyl polyglucosides). In addition, alcohol ethoxylates may undergo oxidation to give by-products (hydroperoxides and aldehydes) that are skin irritants. These classes are commonly used in personal care and cosmetic formulations.

For a homologous series of surfactants there is usually a maximum in skin irritation at a specific alkyl chain length; maximum irritation usually occurs at a C₁₂ chain length. This reflects the maximum in surface activity at this chain length and the reduction in the c.m.c. Anionic surfactants are generally greater skin irritants than non-ionics. For example, sodium dodecyl sulphate, which is commonly used in tooth paste, has a relatively high skin toxicity. In contrast, the ether sulphates are milder and are recommended for use in hand dishwashing formulations. Sometimes, addition of a mild surfactant (such as alkyl polyglucoside) can greatly improve the dermatological properties. Some amphoteric surfactants such as betaines can also reduce the skin irritation of anionic surfactants.

1.8.2

Aquatic Toxicity

Aquatic toxicity is usually measured on fish, daphnia and algae. The toxicity index is expressed as LC₅₀ (for fish) or EC₅₀ (for daphnia and algae), where LC and EC stand for lethal and effective concentration, respectively. Values below 1 mg l⁻¹

after 96 h testing on fish and algae and 48 h on daphnia are considered toxic. Environmentally benign surfactants should, preferably, be above 10 mg l^{-1} .

1.8.3

Biodegradability

Biodegradation is carried out by bacteria in nature. By enzymatic reactions, a surfactant molecule is ultimately converted into carbon dioxide, water and oxides of the other elements. If the surfactant does not undergo natural biodegradation then it is stable and persists in the environment. For surfactants the rate of biodegradation varies from 1–2 h for fatty acids, 1–2 days for linear alkyl benzene sulphonates, and several months for branched alkyl benzene sulphonates. The rate of biodegradation depends on the surfactant concentration, pH and temperature. The temperature effect is particularly important, since the rate can vary by as much a factor of five between summer and winter in Northern Europe.

Two criteria are important when testing for biodegradation: (1) Primary degradation that results in loss of surface activity. (2) Ultimate biodegradation, i.e. conversion into carbon dioxide, which can be measured using closed bottle tests.

The rate of biodegradation also depends on the surfactant structure. For example, the surfactant must be water soluble. Lipophilic amphiphiles such as fluorocarbon surfactants may accumulate in the lipid compartments of the organism and break down very slowly. The initial degradation may also lead to intermediates with much lower water solubility and these degrade very slowly. An example of this is the alkyl phenol ethoxylates, which degrade by oxidative cleavage from the hydroxyl end of the polyoxyethylene chain. This leads to a compound with much smaller EO groups that is very lipophilic and degrades very slowly.

A third important factor in biodegradation is the presence of cleavable bonds in the alkyl chain, which depend on branching. Extensive branching of the alkyl chain tends to reduce the rate of biodegradation. This is probably due to steric hindrance preventing close approach of the surfactant molecule into the active site of the enzyme.

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